

# Calibration of photoelastic modulators in the vacuum UV

Theodore C. Oakberg<sup>\*a</sup>, John Trunk<sup>b</sup>, and John C. Sutherland<sup>b,c</sup>

<sup>a</sup>Hinds Instruments, Inc., 3175 N.W. Aloclek Dr., Hillsboro, OR 97124-7135

<sup>b</sup>Biology Department, Brookhaven National Laboratory, Upton, NY 11973

<sup>c</sup>National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973

## ABSTRACT

Measurements of circular dichroism (CD) in the UV and vacuum UV have used photoelastic modulators (PEMs) for high sensitivity (to about  $10^{-6}$ ). While a simple technique for wavelength calibration of the PEMs has been used with good results, several features of these calibration curves have not been understood. The authors have calibrated a calcium fluoride PEM and a lithium fluoride PEM using the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory as a light source. These experiments showed calibration graphs that are linear but do not pass through the graph origin. A second "multiple pass" experiment with laser light of a single wavelength, performed on the calcium fluoride PEM, demonstrates the linearity of the PEM electronics. This implies that the calibration behavior results from intrinsic physical properties of the PEM optical element material. An algorithm for generating calibration curves for calcium fluoride and lithium fluoride PEMs has been developed. The calibration curves for circular dichroism measurement for the two PEMs investigated in this study are given as examples.

Keywords: Circular dichroism, chiral molecule, photoelastic modulator, synchrotron, UV, vacuum UV.

## 1. INTRODUCTION

Photoelastic modulators (PEMs) are polarization modulation devices that utilize the photoelastic effect to provide modulation of the polarization state of a light beam.<sup>1</sup> The device may be thought of as a waveplate with fixed retardation axis and sinusoidal varying retardation amplitude.

Unlike many other types of polarization modulators, PEMs can be built to cover a wide spectral range: from the vacuum UV (about 120nm) to the mid-IR (about 16 microns). They are used in a wide variety of applications such as Stokes polarimetry, measurement of birefringence, measurement of optical rotation and reflectance difference spectroscopy. The most common application among scientists is the measurement of circular dichroism.

Circular dichroism is a difference in absorption between left circular polarized light and right circular polarized light in a sample.<sup>2</sup> "Natural" circular dichroism occurs in "chiral" molecules, that is, molecules having "right-handed" and "left-handed" isomers (such as dextrose and fructose). The CD effect can be observed in one isomer or the other, but not in an equal mixture of both (racemic mixture). Other (non-chiral) molecules also exhibit CD when exposed to a strong magnetic field (magnetic CD).

CD can be observed associated with the vibrational transitions in molecules. This "Vibrational CD" is observed primarily in the IR spectral region. CD can also be observed with the electronic transitions in molecules ("Electronic CD") and is observed primarily in the UV. Circular dichroism is useful for studying the structure of complex biological and organic molecules such as proteins and DNA.

\*Correspondence: Email: [toakberg@hindspem.com](mailto:toakberg@hindspem.com); Website: <http://www.hindspem.com>; Telephone: 503 690 2000; Fax: 503 690 3000.

Polarization Analysis, Measurement, and Remote Sensing III,  
David B. Chenault, Michael J. Duggin, Walter G. Egan,  
Dennis H. Goldstein, Editors, Proceedings of SPIE  
Vol. 4133 (2000) 2000 SPIE 0277-786X/00/\$15.00

The photoelastic modulator is the preferred technique for studying CD in the spectral range from the vacuum UV (above  $\sim 120\text{nm}$ ) to the mid-IR (up to  $\sim 16$  microns).<sup>3</sup> For measurements in the UV and visible the experiment setup shown in Figure 1 is used.

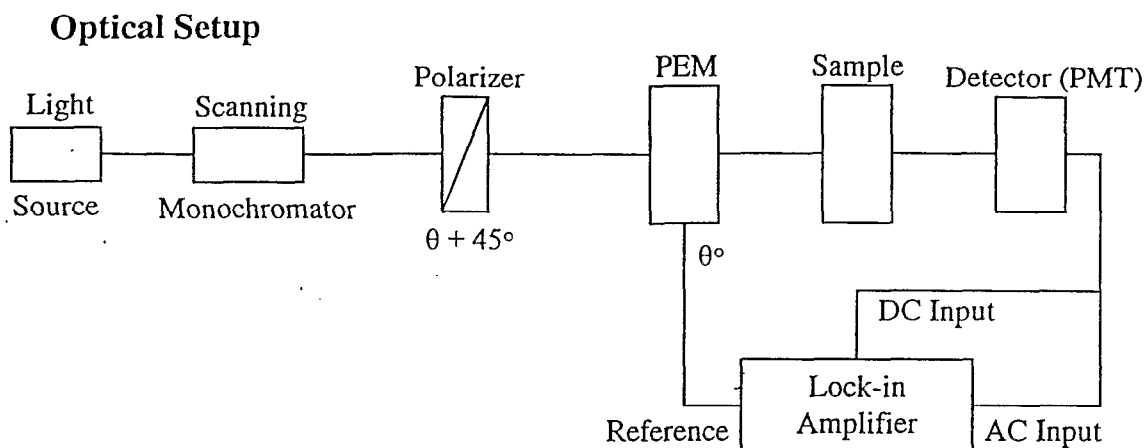


Figure 1. Optical setup for measuring circular dichroism.

Immediately after the PEM, the polarization state of the light switches between left circular and right circular polarization at about 50 kHz. The detector signal consists of a strong DC signal with a weak AC signal at the PEM operating frequency (1f). The circular dichroism is defined as the difference in absorption for the two senses of circular polarized light divided by the average absorption. It is proportional to the ratio of the AC signal to the DC (average) signal or  $V_{1f}/V_{DC}$ . The method is sensitive for circular dichroism to about  $10^{-6}$ .

The CD spectrum of a molecule vs. wavelength is very distinctive, both in regard to the wavelengths at which the effect occurs and the function of the CD signal vs. wavelength. An example of a CD spectrum is shown in Figure 2. Camphor-sulfonic acid is frequently used as a CD standard. It exhibits a comparatively simple CD spectrum.

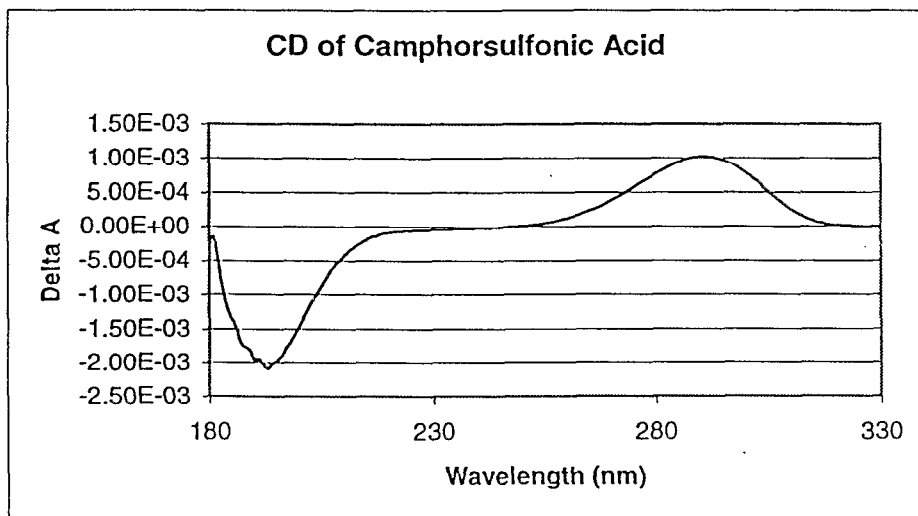


Figure 2. CD spectrum of camphorsulfonic acid

## 2. LIGHT SOURCES FOR ELECTRONIC CD MEASUREMENT

For visible and UV CD measurements, standard laboratory light sources such as Xenon arc lamps may be used. Below about 250nm, however, complications arise. First, calcite polarizers such as Glan-Taylor types cannot be used. Magnesium fluoride polarizers such as Rochon types must be used which provide only a few degrees of separation between the two orthogonally linear polarized light beams. This complicates the setup that may be used for CD measurement by restricting the acceptance angle for light into the polarizer.

Second, the brightness of Xenon lamps decreases rapidly with decreasing wavelength below 250nm. Some commercial CD instruments using arc lamp light sources are able to make measurements down to about 170nm. Deuterium lamps might be used in this region but these are extended sources with relatively low intrinsic brightness.

One light source has excellent characteristics for CD measurements in the UV, including the vacuum UV. This is the synchrotron, a machine for containing a strong electron beam in a ring-shaped path. When the electrons are moving in a magnetic field "synchrotron radiation" is produced. This synchrotron radiation has very high intrinsic brightness, is highly directional, is linearly polarized and has a continuous spectral intensity distribution. It is ideal for CD measurements in the vacuum UV, UV and other portions of the electromagnetic spectrum.<sup>4,5</sup>

The "UV ring" at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory in Upton, New York was used for the UV experiments described in this paper.

## 3. WAVELENGTH CALIBRATION OF CD SPECTROMETERS

Hinds Instruments makes two PEM models for use in the vacuum UV. The optical elements used are 1) calcium fluoride, which operates from the visible to about 140nm, and 2) lithium fluoride, which operates from the near UV to about 120nm.

Both calcium fluoride and lithium fluoride PEMs are calibrated at the factory under atmospheric pressure conditions using visible light. Operation of these PEMs in the UV and vacuum UV raises the following questions:

1. How does the calibration of the PEM change vs. wavelength?
2. How does the PEM calibration change when the PEM is operated in a vacuum?

Previous experiments have been performed at Hinds Instruments to determine calibration vs. wavelength from 250 to 800nm under atmospheric pressure conditions.<sup>6</sup> It has been necessary to extend these measurements from 250nm down into the vacuum UV, to provide calibration information for CD spectrometers operating in this spectral region. The "UV ring" synchrotron at the NSLS has been used for this purpose.

### 3.1 A simple method for CD spectrometer calibration

Wavelength calibration of a CD spectrometer consists of determining the optimum PEM controller setting for measurement of the CD signal as a function of the wavelength of light. In the past, a simple calibration technique has been used, as described below.

1. Place a CD sample with known CD spectrum in the sample position of the CD spectrometer.
2. Adjust the CD spectrometer wavelength to correspond to one of the strong CD lines of the sample.
3. Adjust the PEM controller peak retardation setting until a maximum signal is obtained.
4. Record the PEM setting for this wavelength.
5. Repeat the procedure with CD lines at different wavelengths across the spectral range of interest. (More than one sample species may be required.)

This calibration procedure is simple and effective and has been used successfully in the past. The maximum intensity in theory occurs at a PEM retardation amplitude of 0.293 waves or 1.84 radians. For this argument, the first-order Bessel function  $J_1$  is a maximum. The graph of  $J_1$  vs. retardation amplitude  $A_0$  has a broad peak; so good results will be obtained if the PEM retardation chosen is reasonably close to the optimum value. (Figure 3)

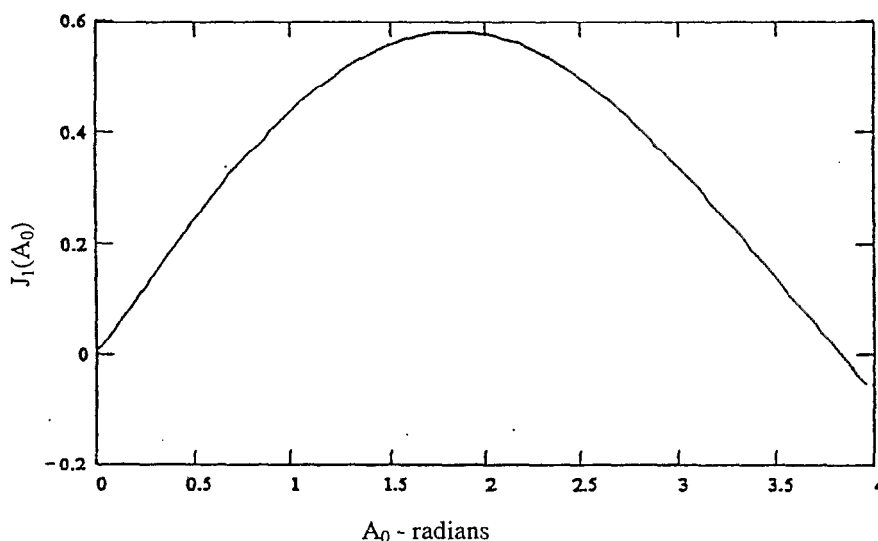


Figure 3. Bessel function  $J_1$  vs. retardation amplitude  $A_0$

Some features of the resulting calibration curves were not understood, and this caused some concern for the experimenters.

### 3.2 Oscilloscope calibration of PEMs

Another technique for PEM calibration has been used since the invention of the device, and is shown in Figure 4. The technique requires a monochromatic light source, two polarizers crossed with the PEM between them, an appropriate detector and an oscilloscope. The detector should have frequency response at least several times the modulator oscillation frequency. The polarizers should be crossed and each should be oriented at 45 degrees with the PEM retardation axis. The PEM provides a reference signal synchronized with the PEM oscillations, which may be used to trigger the oscilloscope.

#### Traditional PEM Calibration Setup

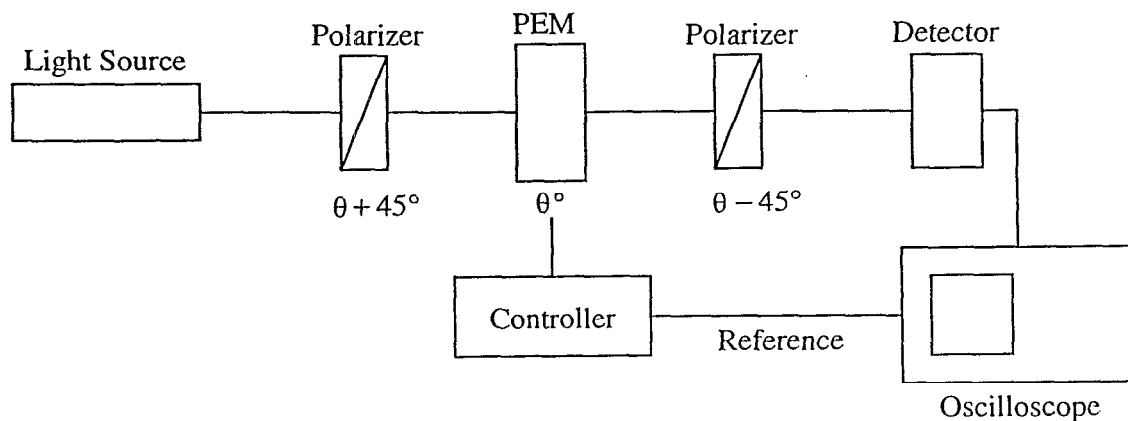


Figure 4. Setup for calibrating a PEM using an oscilloscope.

This setup gives a detector signal at twice the PEM operating frequency, or  $2f$ . For PEM retardation amplitude of half-wave or  $\pi$  radians, the oscilloscope waveform has a unique appearance as shown in Figure 5a. The waveform has a characteristic flat top. If the retardation amplitude is less than half wave, the top appears rounded. (Figure 5b) If the retardation amplitude exceeds a half wave, the waveform tops show a slight dip. (Figure 5c) (Note: depending on the type of detector and the

number of inverting amplifier stages, these waveforms may appear inverted.) With care, the PEM controller can be adjusted to give half-wave retardation amplitude within 1 or 2 %.

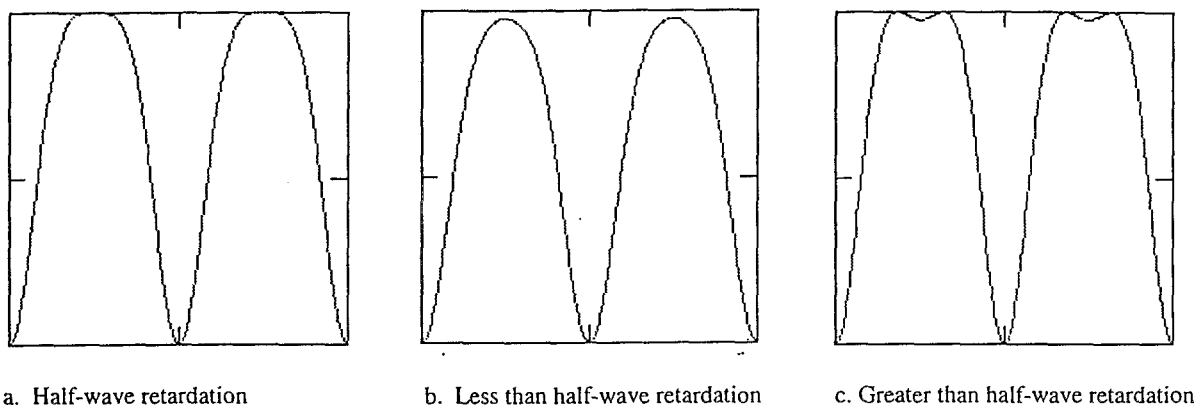


Figure 5. Oscilloscope waveforms for PEM retardation amplitudes near half-wave

This scheme has been adapted for PEM calibration using a synchrotron as a light source. A vacuum monochromator in series with the synchrotron beam provides the wavelength selection needed. Experiments were performed on Beamlines U9B and U11 of the UV ring of the National Synchrotron Light Source. Beamline U9B covered the spectral region from about 165nm to 600nm. Beamline U11 covered the spectral region from 140nm to 300nm. The vacuum monochromators are isolated from the synchrotron ultra-high vacuum and from the CD sample chambers by calcium fluoride or lithium fluoride windows. This allowed operation of the PEM in either a vacuum condition or an atmospheric pressure ( $N_2$  purge) condition. The polarizers used were magnesium fluoride Rochon types.

### 3.3 Calibration of a calcium fluoride PEM using Beamline U9B

The PEM oscillation amplitude is controlled by an internal voltage called  $V_{Control}$ . This may be generated by the internal electronics of the PEM, or may be provided as an analog control signal to the PEM remote input. The calibration experiment consisted of selecting a wavelength of light with the monochromator and order separating filters, then adjusting the PEM controller until the half-wave retardation condition was achieved. (Figure 5a) The internal parameter  $V_{Control}$  was measured with a digital voltmeter.

A calibration of a Hinds Instruments PEM Model I/CF50 was performed using Beamline U9B. The experiment was performed both under vacuum and at atmospheric pressure ( $N_2$  purge). The results are shown in Figure 6.

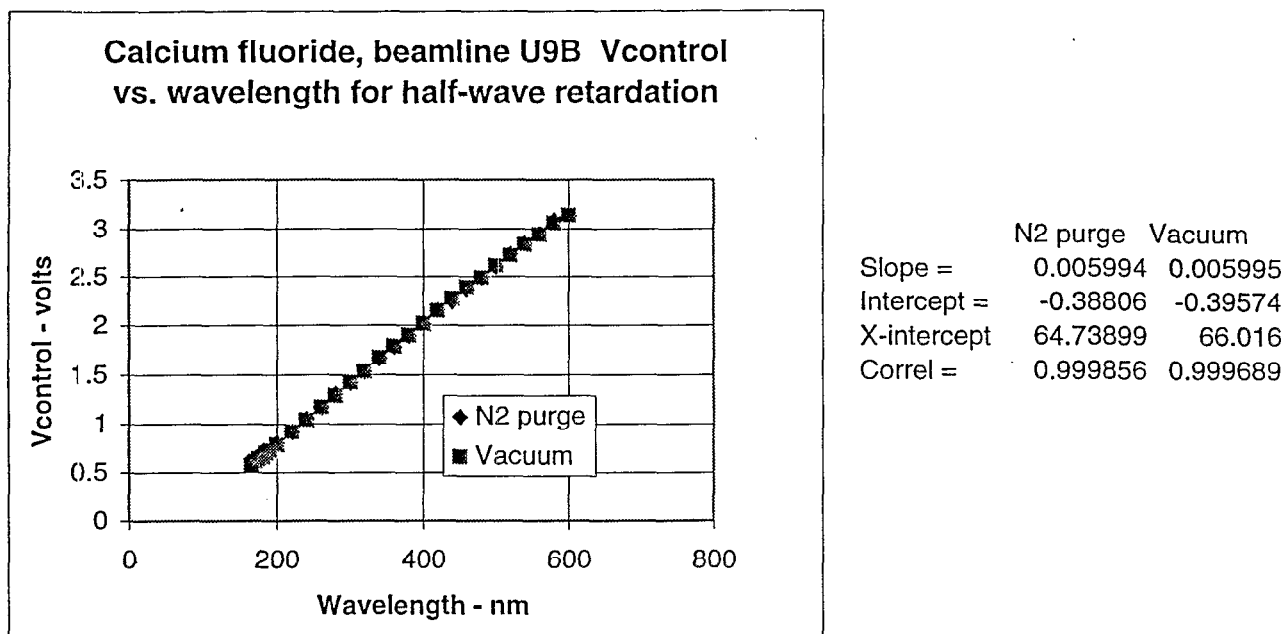


Figure 6.  $V_{\text{Control}}$  vs. wavelength for half-wave retardation, Beamline U9B

Two features of the calibration curves are immediately of interest. First, the graphs are straight lines. Second, the lines do not go through the origin of the graph. The slope and intercept of the calibration curves are given in the table of Figure 6. The intersection of each line with the horizontal axis (X-intercept) is also displayed. (It should be noted that these intersections occur at wavelengths lower than the transmission limit of calcium fluoride.)

It should also be noted that the differences between the calibration curve under vacuum and  $N_2$  purge are slight. This is believed to be the result of careful feedback control of the PEM transducer. (Other electronic drive circuits might not show this characteristic, especially if the PEM transducer is not under feedback control.)

The observation that this linear calibration line does not pass through the origin has been noted by experimenters before and has been a cause of some concern. There are two possible explanations for this behavior.

1. The behavior is an artifact of the electronic circuitry which controls the PEM oscillation amplitude, or
2. The behavior is a consequence of the physical properties of the PEM optical element.

A second experiment is required to decide between these two hypotheses.

### 3.4 Linearity of the PEM electronics

In order to test the linearity of the PEM electronics, a measurement of the relationship between PEM retardation amplitude and  $V_{\text{Control}}$  was made using light of a single wavelength. For this purpose, the optical bench setup of Figure 7 was used. Using a pair of first surface mirrors a laser beam was passed through the calcium fluoride optical element a total of 7 times. (Figure 7 shows 5 passes of the laser beam through the optical element.) Retardation amplitudes of multiple half-waves also show distinctive waveforms, as shown in Figure 8 for retardation of 2 and 3 half-waves.

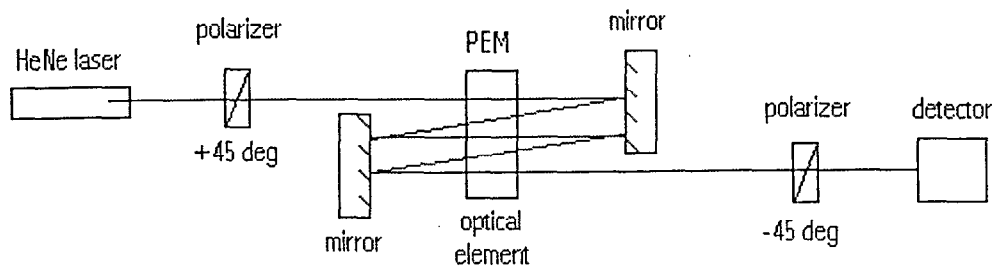


Figure 7. Multiple-pass optical bench setup for testing PEM linearity at a single wavelength

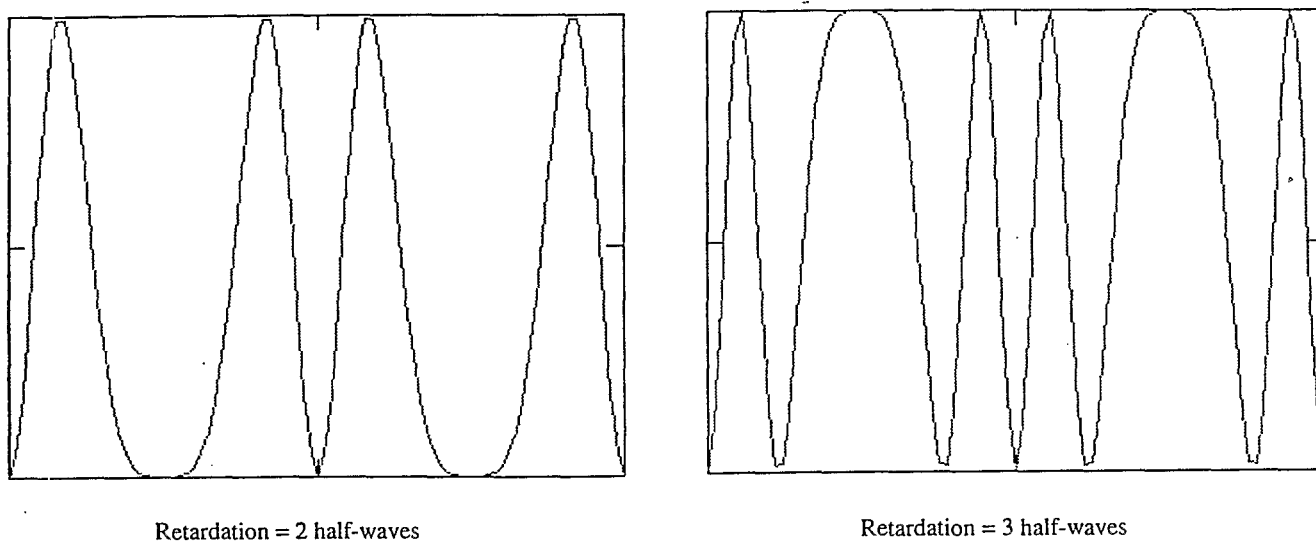


Figure 8. Waveforms for retardation of multiple half-waves

It is thus possible to achieve total retardation of many half-waves. The retardation in nanometers for a single-pass of the laser beam through the PEM vs.  $V_{\text{Control}}$  is shown in Figure 9. (The single-pass retardation was calculated by dividing the total retardation by the number of passes of the laser beam through the PEM optical element.) The laser light wavelength was 594.1nm.

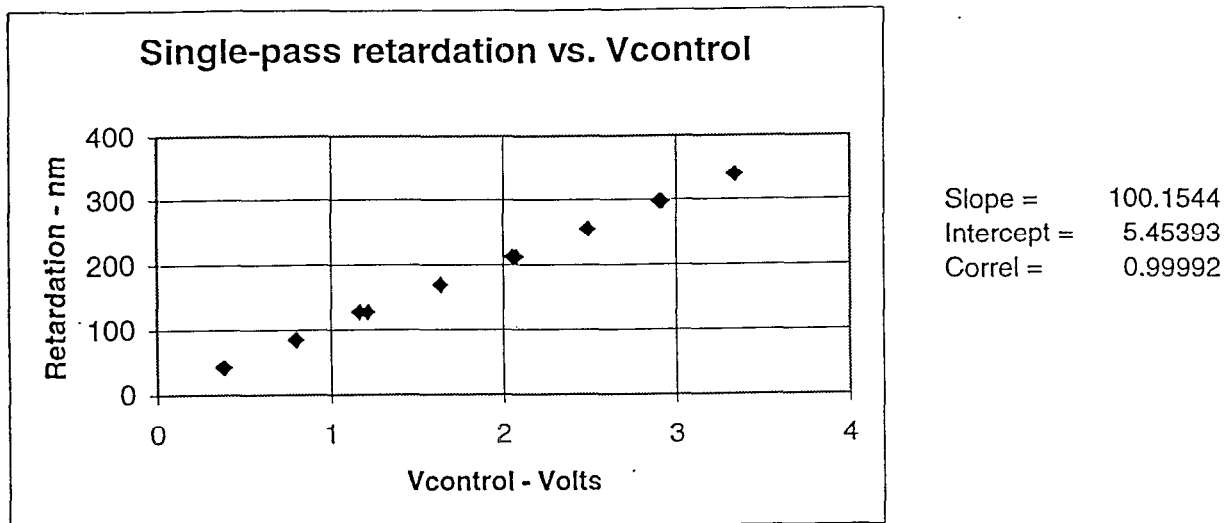
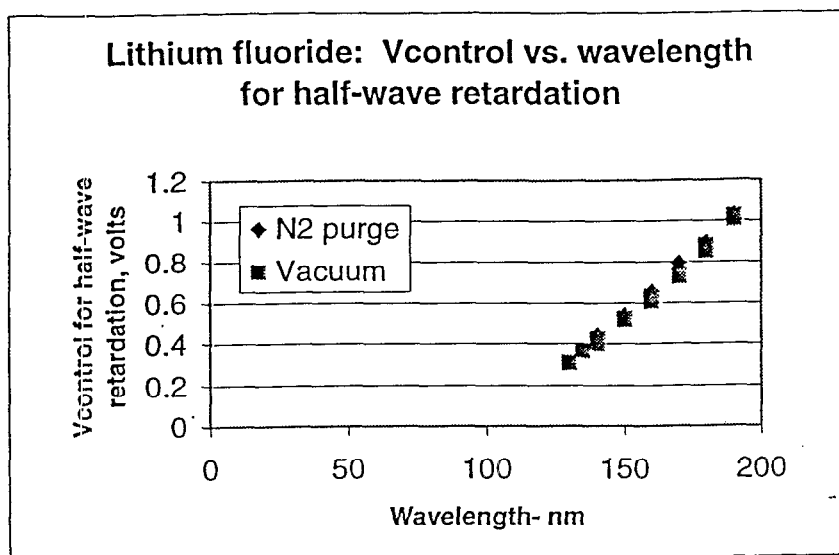


Figure 9. Single-pass retardation vs.  $V_{\text{Control}}$

The relationship between PEM peak retardation and  $V_{\text{control}}$  shows excellent linearity, with the straight-line intercept passing very close to the origin of the graph. The conclusion is that the offset X-axis intercepts of the graphs of Figure 6 is not a consequence of the PEM electronics, but is rather a result of the physical properties of the PEM optical elements.

### 3.5 Calibration of a lithium fluoride PEM using Beamline U11

Lithium fluoride has slightly better transmission characteristics in the deep vacuum UV than calcium fluoride. (Its wavelength cutoff is at 110-120nm or slightly lower than the calcium fluoride cutoff of 125-130nm.) A calibration experiment was performed on a Hinds Model I/LF50 PEM using Beamline U11. The results are presented in Figure 10.



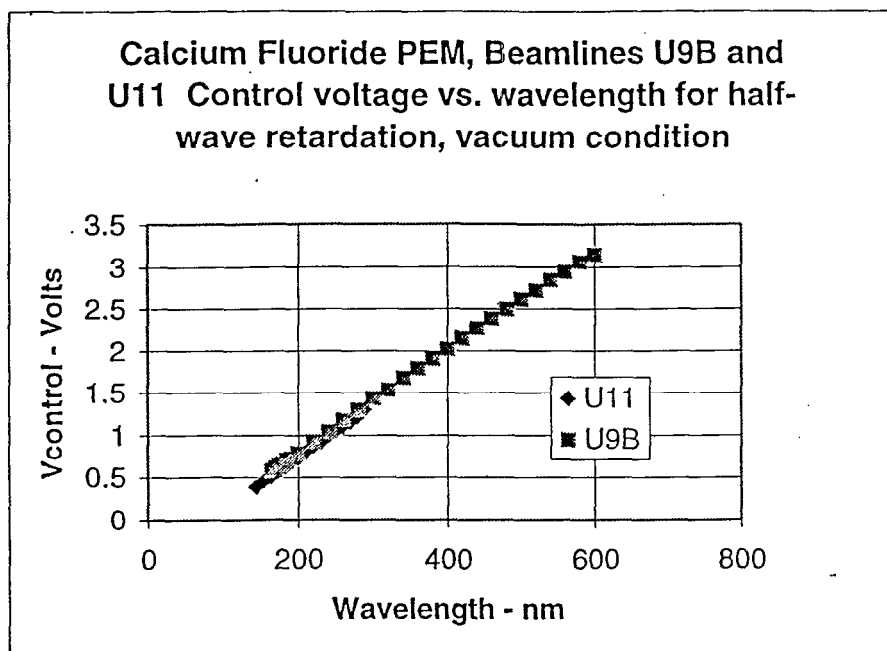
	N2 purge	Vacuum
Slope	0.011589	0.011547
Intercept	-1.19686	-1.20954
X-intercept	103.2727	104.7531
Correlation	0.99699	0.995672

Figure 10.  $V_{\text{Control}}$  vs. wavelength for half-wave retardation, lithium fluoride PEM on Beamline U11

Again the lines do not intercept the horizontal axis at the origin. The graphs, however, now show slight curvature. Again, there is little difference between atmospheric pressure conditions ( $\text{N}_2$  purge) and vacuum.

### 3.6 Calibration of the calcium fluoride PEM on Beamline U11.

A calibration curve of the calcium fluoride PEM was also done on Beamline U11. This calibration graph is shown in Figure 11, along with the calibration curve from Beamline U9B. Although the slopes of the two calibration curves are similar, they are offset and their horizontal axis intercepts are different. The reason for this is not understood. It was noted that the U11 setup has no order-separating filters in it and that stray light may be of concern. (The offset observed could be caused by the presence of light with wavelength shorter than the nominal monochromator wavelength.)



	U9B	U11
Slope=	0.005995	0.006164
Intercept =	-0.39574	-0.49231
X-intercept	66.016	79.87398
Correl =	0.999689	0.99946

Figure 11. Calcium fluoride calibration curves from Beamline U9B and U11.

### 3.7 Calibrating PEMs for CD Measurements

The calibration curves for the calcium fluoride PEM have showed excellent linearity and for the lithium fluoride PEM fair-to-good linearity. Hinds PEMs have also shown little difference between calibration curves obtained under vacuum conditions and atmospheric pressure ( $N_2$  purge). Furthermore, investigation with the calcium fluoride PEM of the linearity of retardation vs. the  $V_{Control}$  parameter show straight-line behavior passing approximately through the origin of the graph.

These observations suggest a method of constructing calibration curves for a PEM to be operated in the UV.

- 1.0 For a given retardation level (e.g. quarter-wave, .293 wave or half-wave), determine the value of a control parameter (e.g.  $V_{Control}$ , controller dial setting, etc.) required to give that level of retardation at one wavelength. This gives one point on a straight-line calibration curve.
- 2.0 The other point on the calibration line is the point  $\lambda = X\text{-intercept}$  and  $(Control\ parameter) = 0$ .

Of course, to make precise calibration graphs using this method, the X-axis intercept must be known with good accuracy. More work needs to be done to resolve the discrepancies between the calibration graphs obtained on Beamlines U9B and U11. Still, either set of data should yield a calibration graph that will give good performance for CD measurements. This is a consequence of the broad peak of the Bessel function  $J_1$ , as shown in Figure 3.

As mentioned before, the optimum retardation for circular dichroism measurement is 0.293 waves or 1.84 radians. An algorithm for deriving a calibration curve for 0.293 waves from the half-wave calibration curve is given in equation 1.

$$V_{Control}(.293\lambda) = V_{Control}\left(\frac{\lambda}{2}\right) \times \frac{1.84}{\pi} = .586V_{Control}\left(\frac{\lambda}{2}\right) \quad (1)$$

Figure 12 shows the derived calibration curves for calcium fluoride and lithium fluoride. As can be seen, there should be little difference in results between the two calibration curves for the calcium fluoride PEM.

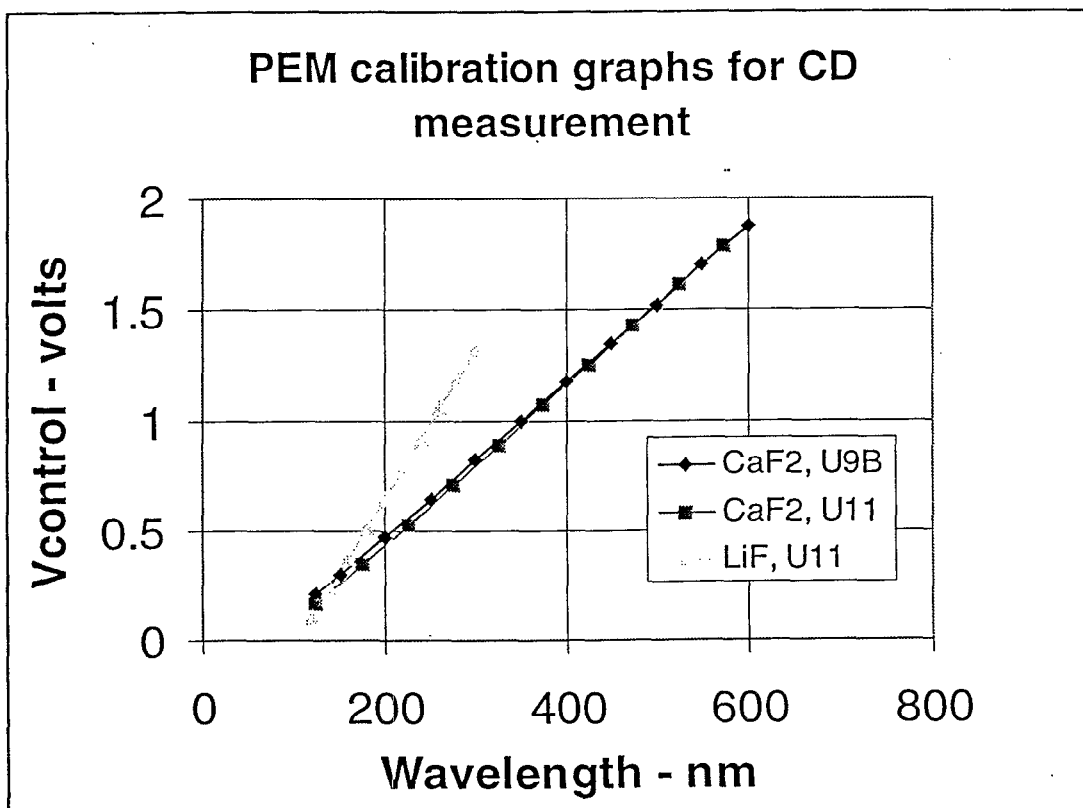


Figure 12. Calibration graphs for calcium fluoride and lithium fluoride PEMs

The internal parameter  $V_{Control}$  has been used as the control parameter for these experiments. In older model Hinds and Morvue PEMs,  $V_{Control}$  is established by a 10-turn potentiometer with a 10-turn dial. The dial reading is also a suitable control parameter for calibration purposes.

#### 4. ACKNOWLEDGMENTS

Research was performed (in part) on Beamlines U9B and U11 of the National Synchrotron Light Source, which is supported by the Office of Biological and Environmental Research, USDOE. The NSLS is supported by the Office of Basic Energy Sciences, USDOE.

Hinds Instruments, Inc. also supported this research.

## 5. REFERENCES

1. J.C. Kemp, "Piezo-Optical Birefringence Modulators: New Use for a Long-Known Effect," *J. Opt. Sci. Amer.*, **59**, pp. 950-954, 1969.
2. A.F. Drake, "Optical Activity and the Spectroscopy of Chiral Molecules", *European Spectroscopy News*, **69**, pp. 10-17, 1986.
3. A.F. Drake, "Polarization modulation—the measurement of linear and circular dichroism", *J. Phys. E: Sci. Instrum.*, **19**, pp. 170-181, 1986.
4. J.C. Sutherland, E.J. Desmond and P.C. Takacs, "Versatile Spectrometer for Experiments Using Synchrotron Radiation at Wavelengths Greater than 100nm", *Nuclear Instruments and Methods*, **127** pp. 195-199, 1980.
5. P.A. Snyder, "Status of Natural and Magnetic Circular Dichroism Instrumentation Using Synchrotron Radiation", *Nuclear Instruments and Methods in Physics Research*, **222**, pp. 364-371, 1984.
6. Oakberg, T.C., "Relative variation of stress-optic coefficient with wavelength in fused silica and calcium fluoride", *Polarization: Measurement, Analysis, and Remote Sensing II*, *SPIE Vol 3754*, pp. 226-234, 1999.